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THE MERCURY ARC IN DYE TESTING

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By OSCAR R. FLYNN
Consulting Textile and Dye Chemist

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FADING LAMPS

By OSCAR R. FLYNN
Consulting Textile and Dye Chemist

How the Mercury Arc Was Made to Imitate Sunlight

A paper read at the meeting of the Rhode Island Section of the American Association of Textile Chemists and Colourists on October 19, 1923.

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THE ACTION OF LIGHT ON COLOURING MATTERS

By Wm. HARRISON
M. Sc. Tech., etc.

Reprinted in part from a paper read at a meeting of the Society of Dyers and Colourists, March 22, 1912, and published in the Journal of the Society of Dyers and Colourists, Vol. 28, No. 7, pages 225-36, July 19, 1912.

Certain extraneous material together with the tabulated data has been omitted where indicated, the omissions, however, being of such a nature as in no wise to affect the interpretation of the parts reprinted.

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The Mercury Arc Lamp in Dye Testing

OSCAR R. FLYNN

Anomalous Effects of the Mercury Arc Explained—Oxidation vs. Reduction Fading—Reversals in Relative Fastness of Direct and Basic Colors—Method of Tempering Light from the Mercury Arc to Give the Effect of Sunlight—Uses of the Untempered Arc

The effect of light on coloring matter, bringing about its alteration or destruction, like other photo-chemical effects, is very little understood; and for this reason the testing of dyes for light fastness is largely in the empirical stage.

For a long time the chief difficulty in the way both of the scientific study of light effects as well as the practical testing of dyes for light fastness, has been the lack of a suitable source of radiant energy; but this difficulty has been largely overcome, by the discovery of the mercury vapor arc and by the improvements in the technique of working with fused quartz, which has made it practicable to house the arc within walls which permit its radiant energy to escape.

The intervention of the World War put a stop to many lines of scientific investigation not of immediate application and among other things turned the attention of the dye chemist toward the chemistry of dye construction rather than dye destruction. Just at present there seems to be a revival of interest in those problems which concern the fastness of dyes, and especially in problems of light fastness. This would of course make it timely to take up again the question of the fitness of the mercury arc for dye testing.

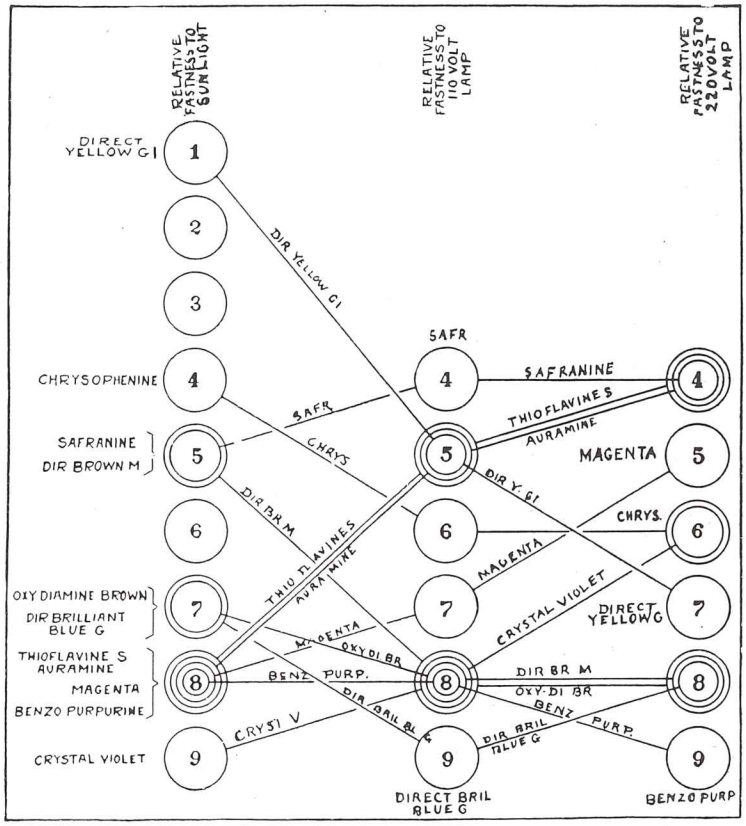


Fig. 1—Effect Produced on Relative Fastness of Direct and Basic Colors by Increase in Intensity of Fading Light. Interpretation of Harrison's Results

Mercury Arc Light

The mercury arc is peculiar in that such a large proportion of the radiant energy generated by the resistance of the mercury vapor to the passage of the current is of the short wave rapid vibration kind to which the eye has not been attuned, and which is therefore invisible light. Being more refrangible than the visible violet rays, its spectrum falls beyond the spectrum of the violet where its presence is made known by photography and by its fluorescent effects on a screen coated with anthracene or other fluorescent substance. Because of its position in the spectrum we have the name ultraviolet.

This kind of radiation (the ultra violet) is especially active in bringing about chemical change. It is the presence of a small proportion in sunlight which is responsible for most of the chemical effects of the sun such as sunburn, bleaching of linen, and the fading of dyes.

The presence of a much larger proportion in the mercury light makes it more powerful in the production of all these effects.

Owing to the fact that calcium and lead absorb ultra violet radiation, especially the shortest waves which are the most active chemically, the mercury arc enclosed in glass does not exhibit its most powerful chemical effects, and it is only when the arc operates within a transparent chamber of purest quartz that these actinic rays stream forth in fullest intensity and become fully available for the production of fading and other chemical effects.

Use in Dye Testing

Various investigators have experimented with the quartz tube mercury light and have noted its destructive effects on many compounds, including the colored organic substances used as dyes, and it has generally been concluded that the fading energy from this source was not only stronger than sunlight but intrinsically different in its effects. In spite of this conclusion its quick action and ready availability has caused it to be extensively used in dye testing, each user making such allowance and corrections as his experience with his own line of work have shown to be necessary.

In my own work with dyed cotton fabrics at the Waldrich Bleachery, I made it a practice to expose to the mercury light samples of every dyeing made in the regular course of work. The dyeings were pasted on sheets of paper in narrow strips, about twenty to the sheet, and exposed usually for half an hour in such a way as to bring one-third of each strip under the action of the light. The sheets were then exposed to sunlight in such a way that another third of each strip was acted upon by sunlight, the time of the sunlight exposure being regulated by the behavior of a standard dyeing of scarlet 8BS placed with each set of dyeings. The sunlight exposure was continued until this standard showed the same degree of sunlight fading as of mercury light fading. In other words the exposure to sunlight was allowed to go on until balanced fading had been registered on the standard selected.

Peculiarities in Fading

By a study of these sheets I was able to pick out a number of examples of departure from the norm of balanced fading in one direction or the other. I noticed that basic dyes on antimony tanned cotton were faded much more heavily by the sun than by the mercury light and that many of the so-called light fast cotton dyes, the L brands, were out of balance in the opposite sense.

It was also noticeable that exposure to the strong mercury light produced effects which were not seen at all in the sun fadings. For example, chrysophenine and chloramine yellow were darkened and indanthrene yellow G assumed a distinctly greenish tone. Some of the light fast cotton colors exhibited a change in shade toward the purple. This was distinctly the case with Solamine red 8BL. These abnormal changes in tone disappeared, however, after the dyeings had rested for a sufficient time in the dark, and whatever fading could then be noticed would not be distinguished from sunlight fading.

Selective Radiation

In attempting to find a reasonable explanation for these peculiarities, both of unduly rapid or retarded fading as well as abnormal changes in color, I encountered the term "selective radiation." A hot solid usually gives off a continuous mass of radiation, the amplitude of the waves gradually decreasing as they become shorter. As the temperature is increased additional and finer waves are continually being added to the mass. A heated gas, however, dissipates its energy in certain selected wave lengths. The spectrum of the hot solid is continuous, decreasing in intensity toward the violet, while the spectrum of the hot gas is discontinuous, appearing as a number of bright lines in different parts of the spectrum.

This selective radiation of gases extends beyond the visible part of the spectrum into the ultra violet. Now it has been argued that the peculiar effects observed in dyes exposed to the radiations from hot mercury vapor result from selective absorption of the selective radiation which it gives off, especially the ultra violet part.

To make clear just what is involved in this explanation we may make use of an illustration drawn from the theory of sound. The waves given off by a musical instrument such as an organ pipe are distinctly selective in character, consisting of waves corresponding to the pitch and a certain number of overtones. Such an organ pipe produces a sound spectrum which corresponds to the spectrum from a hot gas.

Now let us represent the dye molecule by a tuning fork to which we will imagine certain pith balls have been lightly fastened to produce an aggregation which is capable of being broken up. When the organ pipe sounds the tuning fork will be disturbed or not according to whether the pitch of the fork corresponds to the pitch of the pipe or its overtones. If it does correspond to one of the more powerful waves it will be set in strong sympathetic vibration and the pith balls will be thrown off, symbolizing in this way the decomposition of the dye mole-

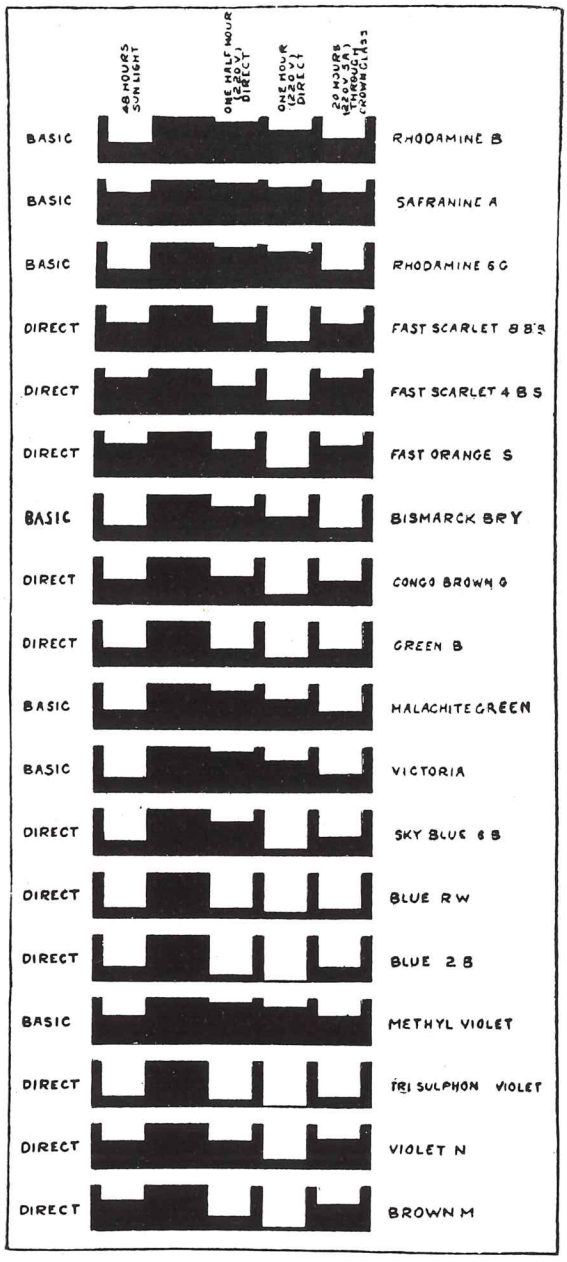


Fig. 2—Equalization in Rates of Fading Brought About by Tempering of Mercury Radiation with Crown Glass; Relative Fading Shown by Depth of "Cut." Original Results

cule by selective absorption of selective radiation.

Now let us imagine a sound possibly equal or greater in energy to emanate from, let us suppose, a small waterfall. This continuous roar will correspond to the spectrum of the hot solid and will, of course, contain waves which synchronize with the tuning fork, but as they represent such a small part of the total energy the resulting effect will be much less than that produced by the organ pipe and the pith balls will not be so quickly thrown off; they may in fact not be thrown off at all.

Effect of Fibre

The obvious fallacy of the selective radiation theory is in supposing that the fading effect is primarily a decomposing action of the light upon the dye and ignoring the fact that the substances in contact with the dye have more effect in determining the fastness of the dye to light than has the kind of light.

It has long been known that the so-called direct cotton dyes are in many cases much faster when dyed upon wool than when dyed upon cotton. Even congo red, which represents one of the lowest degrees of fastness as a cotton dye, is quite a fast color when dyed upon wool. Also it has been known for a long time that many dyes which fade quite easily in the air do not fade in vacuum.

The best working theory of fading as applied to colors dyed upon cotton appears in a paper published in the "Journal of the Society of Colourists and Dyers," July, 1912, by William Harrison. The title of this contribution is "The Action of Light on Coloring Matter." It is a paper well worth reading in its entirety.

Harrison had observed just as others before him had done, that the quartz tube mercury light produced effects which differed from those of sunlight, not only in quickness as a whole, but in relative quickness as well. He found in other words that fastness tests made with the mercury lamp gave different results from those obtained by sunlight exposures.

Harrison's Experiments

He made, however, this additional discovery, namely, that the departure from normal sunlight fading increased as the speed with which the fading took place was increased, or in other words, that there was an inverse relationship between quickness of fading and normality of fading.

In order to throw light on this inverse relationship, he carried out a number of experiments which tended to show that the fading produced by light was the result of at least two actions more or less antagonistic, that is, the oxidizing action of the air and the reducing effect of the fibre. His experiments also tended to show that the reducing effect was accelerated much more than the oxidizing effect by an increase in the intensity of the fading energy.

He investigated the action of mercury light alone on a representative selection of dyes by exposing them in evacuated and sealed quartz tubes to the light, the dyes being filmed on glass for this pur-

pose instead of being dyed on the usual fibre of cotton, silk or wool.

As a result of this experiment he was able to reaffirm what has long been generally believed by close students of the subject, namely, that dyes do not fade in the absence of air or of fibre. Absorption of light by the dye, selective or otherwise, certainly has little if any influence in fading; that is, fading is a chemical reaction and not merely a chemical decomposition.

The same collection of dyes filmed on glass as before gave a different set of results when exposed to the mercury light in the presence of air. Especially it should be noted that the two direct cotton colors used, colors which would ordinarily be classed as fugitive, did not fade, while the two basic colors did fade, revealing the fact that oxidation was the cause of the fading of the latter while the fading of the direct colors as we ordinarily encounter it must be due to some other cause.

Direct colors when dyed on cotton in the usual way and exposed to strong mercury light in the absence of oxygen, the access of the ultra violet rays and the exclusion of air being secured as before by sealing in quartz, were found to fade. That this fading was caused by reduction was made evident by the discovery that the cotton itself had been oxidized where it had been in contact with the faded dye.

A well known vat color which turns blue on reduction was also found to be affected by cotton under the influence of the mercury light and in the absence of air, and to reveal by its change in color that the action was a reducing one. The dye in question, indanthrene yellow (the same dye already referred to) was found to turn green when acted upon by the light, the green color disappearing when the tube was opened and the air readmitted.

Although basic colors are capable of forming leuco dyes by reduction, and although these leuco dyes are more or less colorless, it could not be discovered that crystal violet underwent any change when exposed on cotton and in the absence of the air to the strong mercury light. It should be noted, however, that the crystal violet was not directly in contact with the cotton, as it had been dyed in the usual way on a tannin mordant.

Light Intensity

Harrison also carried out some experiments which tend to show that the reducing action of light is proportional to the intensity. He found for example that the greenish color developed in the indanthrene yellow on cotton was greater under the action of the 220-volt arc than under the 110-volt arc, a condition of equilibrium seeming to result. In the presence of air there was no noticeable effect produced by the 110-volt arc, due as he explains to the fact that the air reoxidized the blue reduction compound as fast as it was formed; but in the case of the 220-volt arc the reduction was too rapid for the air to counteract its effect so some greenish color developed.

A similar result was obtained with methylene blue which in this case, and unlike the crystal violet, was dyed directly on the cotton, if we can properly call cotton stained with methylene blue dyed.

Methylene blue so dyed or stained upon cotton was found to fade slowly in sunlight and more rapidly under the 110-volt arc, but there was no evidence of the formation of leuco dye; the fading was evidently by oxidation just as in the case of the dye exposed on glass. However, when the 220-volt arc was put into action there was unmistakable evidence that the fading was at least partly reduction. It was found that the faded portion contained some leuco methylene blue which could be made to show itself quickly by wetting the faded spots with ammonia water which stimulated the reoxidation.

Direct cotton dyes curiously enough were found not to be affected by even prolonged exposure to sunlight on cotton in the absence of air. This exposure was carried out in evacuated tubes, which were in this case of glass, but that fact would have little bearing on the subject as we know that under ordinary circumstances and in the presence of air, these same dyes fade quite readily in sunlight, even though it is filtered through glass.

He found, however, that a preliminary treatment of the cotton with acids or with oxidizing agents brought it into a condition so that direct dyes would fade when dyed upon the cotton so modified and then exposed to sunlight in the absence of air. From these results he concludes that the fading of direct colors under ordinary circumstances, that is, in sunlight or under fading light of about the same intensity, is due, not directly to the reducing action of the cellulose, but due rather to the action of the cellulose which has been modified by the oxidizing action of the air under the action of the light, in other words, due to the action of oxycellulose.

This in itself is not a far-fetched conclusion, as it is quite certain that cellulose does become converted into oxycellulose by the action of air stimulated by sunlight, and furthermore cellulose once oxidized becomes prone to still more oxidation; that is, oxycellulose is a much better reducing agent than unmodified cellulose. To sum up, then, some of the main conclusions of Harrison's article, we have the following:

Direct colors containing an azo linking *fade* under strong light in the absence of oxygen through the reducing action of cellulose; under weak light,

in the presence of oxygen by the reducing action of oxycellulose. Colors which do not contain azo linkings and which cannot be destroyed by reduction, fade by oxidation.

Reversal of Relative Fastness

The influence of the two kinds of fading; namely, fading by oxidation and fading by reduction, in causing a reversal of the relative fastness of direct and basic colors when tested by strong mercury light, is shown in the chart at Fig. 1. This chart embodies the results in one of Harrison's tables.

The results of the action of three kinds of light on nine colors dyed on cotton are shown. Six of these are direct colors and three of them are basic, but the result is the more striking because of the behavior of one of the direct colors which happens to be one of those yellows related to primuline, which cannot be destroyed by reduction and which is here seen to line up with the basic colors not destroyed by reduction. The dye in question is thioflavine S.

The exposure to sunlight, 110-volt mercury light, and 220-volt mercury light was continued in each case until benzo-purpurine was faded to practically the same degree under all three lights, as shown by the fact that the benzo-purpurine line is nearly straight. This was not intentional, however, on the part of the experimenter and had any dye been deliberately chosen to furnish a standard of comparison it would have been better to have selected one of the basic dyes and to have timed the exposures so that this basic dye showed the same fading under all three lights, as the basic dye probably fades more nearly in direct proportion to the strength of the fading light than do direct azo colors like benzo-purpurine.

Nevertheless, taking the results just as they are given it is quite easy to see that there is a general parallelism between the lines representing the behavior of the direct azo colors which are destroyed by reduction, and a similar parallelism between the lines corresponding to the basic and the non-azo direct colors, which are the ones not capable of being destroyed by reduction and represent the type which fades by oxidation.

A conspicuous example of reversal of relative fastness as between the reducible and non-reducible types of fading is seen first in the case of the three yellow dyes, which exhibit a fastness of five under the 110-volt light. The direct azo yellow, which is very much faster than the basic auramine and the direct dyeing non-azo thioflavine S under sunlight, shows relatively fugitive compared with two colors when tested under the 220-volt lamp. A similar relationship is also observed between oxydiamine brown, brown M, and benzo-purpurine, three direct dyeing azo colors on the one hand, and the basic dye crystal violet on the other. Although the differences in fastness shown under sunlight and under the 220-volt light are not so great as in the case of the yellows, the reversal is just as evident.

This reversal of the relative rates of fading as between the dyes which come under the classification of dyes fading by reduction and those fading by oxidation, suggested very strongly that in comparing dyes belonging to these two classes it will be necessary to cut down any strong artificial fading light to an intensity comparable with sunlight, either by lessening the voltage, increasing the distance, or by interposing transparent filters of glass capable of absorbing some of the ultra violet light.

Tempering Mercury Arc Light

It was decided to make the first tests with screens of thin crown glass of different thicknesses. In preparation for the tests a large number of swatches dyed with representative direct and basic colors were exposed at the same time, so as to register the same intensity and amount of sun fading on a small part of each swatch, the rest being carefully covered from the action of the sun. The exposures were made from 9 A. M. to 3 P. M. on clear days only, and at the end of forty-eight hours of sun exposure, a sufficient number of the colors registered a degree of fading which warranted going on to the next step. This consisted first in cutting off strips showing some of the faded and unfaded portions of the swatches selected.

These strips were exposed to the action of the mercury vapor lamp of 220-volts at a distance of nine inches in such a way that the light, after passing through one and one-quarter millimeters of crown glass (microscope slides), registered fading on the end opposite to that faded by the sun, the sun-faded portion and the intervening portion being protected by a metal screen.

It was found that after twenty hours of continuous exposure to the mercury light, as described, all of the dyes both direct and basic registered a degree of mercury light fading which almost exactly balanced that of the sun, so much so that it was not thought necessary to make further tests with glass of different thickness. It was thought, in fact, more important to extend these results to dyes on wool and silk, and to that end steps were at once taken to register sunlight fading on a number of silk and woolen swatches to be used in the same way as the cotton swatches and thus definitely determine whether the same sort of tempering would serve to equalize the fading for dyes on these fabrics.

To illustrate as well as possible the effect of the fading tests on the cotton swatches a chart (Fig. 2) has been prepared in which the dyes are represented as rectangular strips, the degree of fading being represented by a part of the strip cut out. As already explained, the sunlight fading is at one end and the tempered mercury light fading at the other. The intervening fadings represented show the effect

of one-half hour and one hour fading by direct mercury light registered on the strips after the regular test, so as to show the reversal of relative fastness between the direct and basic dyes when exposed to the strong untempered mercury light.

Before the experiment with the one and one-quarter millimeters of crown glass was made it was our practice in the use of the mercury light for testing purposes to make all tests in groups so that for each dye being tested there were several others of known fastness and belonging to the same class to act as standards. By the use of these standards it was possible to draw very reliable conclusions from the results and get them quickly. From now on, it is our intention to proceed somewhat as follows in making light tests of colors dyed on cotton:

Dyeings will be exposed first to the strong 220 mercury vapor arc light at a distance of 18 inches for a period of about three hours. Any dyes which stand up under this treatment will be classed forthwith as cotton dyes of the highest degree of fastness. However, dyes which do not come through this test satisfactorily will not be condemned, but will be given another chance. They will be exposed to the 220 mercury light at a distance of nine inches, the light being allowed to filter through one and one-quarter millimeters of crown glass. This test will be considered as equivalent to direct sunlight exposure, each hour of lamp exposure to be counted as equal to 2.4 hours of direct December sun at the middle part of a clear day. It will be possible by this procedure in many cases to get a positive answer within three hours, especially with dyes not capable of being destroyed by reduction. Where reducing effects interfere and it becomes necessary to make use of the tempered arc, the answer will still be forthcoming within a period of 24 hours.

In conclusion it should be stated that in selecting the fading effects of the mercury light on dyed cotton for investigation the intention was to attack the most difficult part of the problem of fading first. Taking into consideration the known fact of the greater stability of the cotton dyes on wool and silk, it does not seem too much to assume that even a less degree of tempering will be found to correct any irregularities which may exist here and cause the mercury arc fadings on the animal fibres to parallel those of the sun. The results of tests along these lines will soon be ready and will furnish material for a future communication.

Fading Lamps

By OSCAR R. FLYNN

How the Mercury Arc Was Made to Imitate Sunlight

Resume of Results Previously Printed—New Experiments with Silk and Wool—Behavior of Chrome Colors—The Equalizing Effect of Crown Glass—Results Expected from Cobalt-Nickel Glass—Method of Maintaining Constant Intensity of Fading Energy

The Need of a Rapid Method for Testing Light Fastness

Several years ago we had occasion to dye in light-fast cotton colors a quantity of "repp" to be used for draperies. We had promised delivery on part of the order at such an early date that there was not sufficient time to submit preliminary dyeings to sunlight, the difficulty being further increased by the fact that some of the dyes which we contemplated using were of American make and by us hitherto untested in the combinations which we expected to make. At this juncture we decided to make use of a quartz mercury arc lamp and to expose our preliminary dyeings to its powerful rays along with the customer's samples. This we did and, later exposing the same dyeings to sunlight, found happily that we had not been misled.

Comparison of the Mercury Arc Fadings with Sunlight Fadings

The comparative light tests started in this way were continued. For a long time each dyeing made in the laboratory was subjected to a comparative light test. The dyeings were pasted on sheets of paper, about twenty strips to a sheet, and exposed to the rays of the mercury arc in such a way that a half-hour's fading was registered on a third of each strip. They were then exposed in a south window so that another third of each strip became faded by sunlight, the exposure being continued from day to day until the sun fade on an "indicator strip" of Scarlet 8BS, which formed a part of each set, was made to balance the mercury arc fade on this indicator strip.

These doubly faded strips afforded material for a preliminary study of the mercury arc fadings in comparison with sunlight.

Peculiarities of the Mercury Arc Fade on Dyed Cotton

An examination of these fading sets shows that direct cotton dyes on cotton have faded many times faster by mercury light than by sunlight, but that the fadings for the most part "balance." The balance is, of course, conditioned by the fact that a direct cotton dye—viz., the Scarlet 8BS—was used as an indicator.

The so-called L brands of cotton dyes (dyes of superior light fastness) do not show balanced fadings, but are faded proportionately more by the mercury arc than by the sun. In passing, it might be stated that at the time the work was being done it was noted that some of these dyes, especially the red, exhibited a purplish effect in the mercury arc fade which disappeared, however, in the dark, leaving a fade of the same general character as the sun fade. Some of the yellows also showed temporary darkening, which also disappeared after the strips were removed from the vicinity of the lamp.

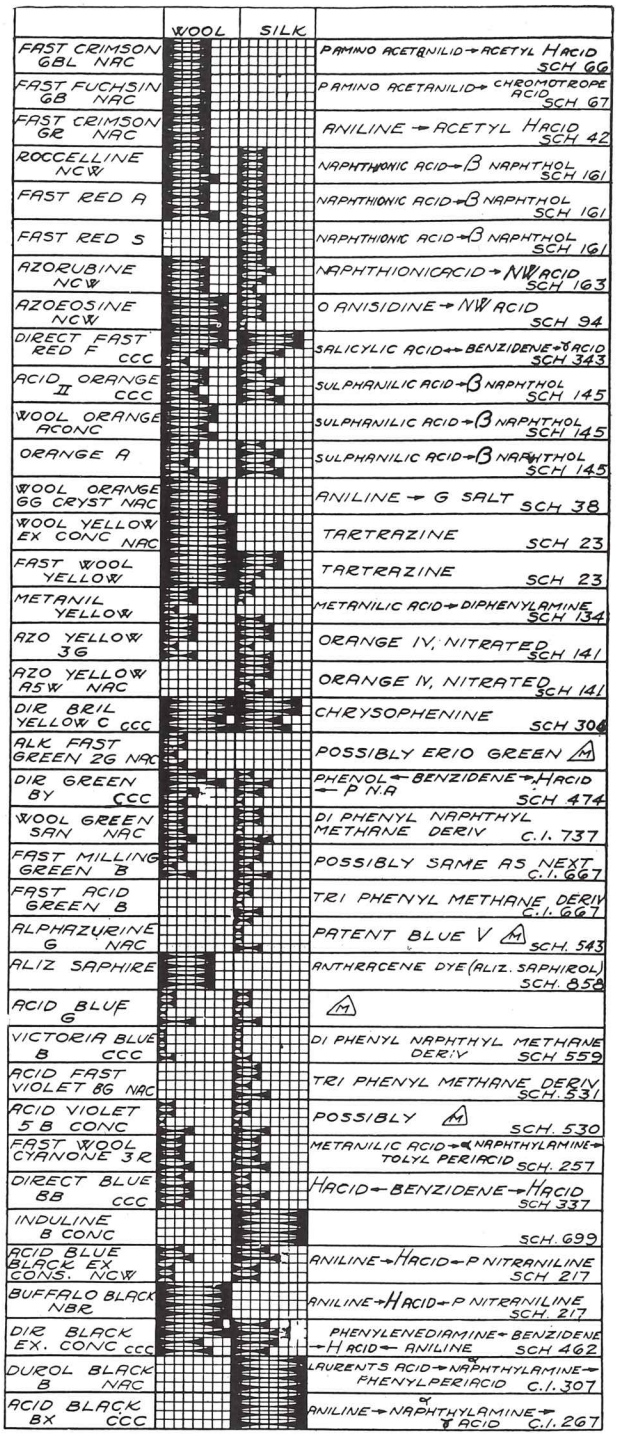
In the case of the majority of the sulphur colors, the time was too short to register any noticeable change. Sulphur Black is seen, however, to have faded like the L brands of cotton colors, proportionately more under the mercury arc than in the sun. Columbia Black FF shows exactly the reverse effect.

The greatest variation, however, is found in the behavior of the basic colors. Without exception, those tested were found to have faded very materially less under the mercury arc than in the sun, owing to the fact, already noted, that a direct dye was used as the standard.

The order of fastness of the cotton and sulphur dyes by the mercury arc is practically the same as the order of fastness by sunlight, but the differences in fastness between the various dyes are less. The basic dyes, however, if inserted in these lists would be near the top of the first list and near the bottom of the second.

Tentative Explanation of the Reversal in Fastness of the Basic Dyes

In attempting an explanation of the peculiar behavior of the basic dyes under the mercury arc, it became apparent that there must be at least two actions going on during fading, which we may call "A" and "B" effects. Both of these actions are accelerated by an increase in the intensity of the fading light, the "A" effect, however, being much more accelerated than the "B." The "A" effect is the one more prominent in the fading of the direct colors; the "B" seems to predominate in the fading of the basic colors. Recalling the fact that the majority of the direct cotton colors are easily destroyed by reduction, and that the basic colors when not too violently reduced are generally capable of being restored by subsequent oxidation, it naturally occurred to me (as it has to others) that the "A" effect was a reducing


WOOL
SILK
FAST CRIMSON GBL NAC
P AMINO ACETANILID → ACETYL H ACID SCH 66
FAST FUCHSIN GB NAC
P AMINO ACETANILID → CHROMOTROPE ACID SCH 67
FAST CRIMSON GR NAC
ANILINE → ACETYL H ACID SCH 42
ROCCELLINE NCW
NAPHTHIONIC ACID → β NAPHTHOL SCH 161
FAST RED A
NAPHTHIONIC ACID → β NAPHTHOL SCH 161
FAST RED S
NAPHTHIONIC ACID → β NAPHTHOL SCH 161
AZORUBINE NCW
NAPHTHIONICACID → NW ACID SCH 163
AZOEOSINE NCW
O ANISIDINE → NW ACID SCH 94
DIRECT FAST RED F CCC
SALICYLIC ACID ← BENZIDENE → α ACID SCH 343
ACID II ORANGE CCC
SULPHANILIC ACID → β NAPHTHOL SCH 145
WOOL ORANGE ACONC
SULPHANILIC ACID → β NAPHTHOL SCH 145
ORANGE A
SULPHANILIC ACID → β NAPHTHOL SCH 145
WOOL ORANGE GG CRYST NAC
ANILINE → G SALT SCH 38
WOOL YELLOW EX CONC NAC
TARTRAZINE SCH 23
FAST WOOL YELLOW
TARTRAZINE SCH 23
METANIL YELLOW
METANILIC ACID → DIPHENYLAMINE SCH 134
AZO YELLOW 3G
ORANGE IV, NITRATED SCH 141
AZO YELLOW A5W NAC
ORANGE IV, NITRATED SCH 141
DIR BRIL YELLOW C CCC
CHRYSOPHENINE SCH 30
ALK FAST GREEN 2G NAC
POSSIBLY ERIO GREEN M
DIR GREEN BY CCC
PHENOL ← BENZIDENE → H ACID ← P N A SCH 474
WOOL GREEN SAN NAC
DI PHENYL NAPHTHYL METHANE DERIV C.I. 737
FAST MILLING GREEN B
POSSIBLY SAME AS NEXT C.I. 667
FAST ACID GREEN B
TRI PHENYL METHANE DERIV C.I. 667
ALPHAZURINE G NAC
PATENT BLUE V M SCH. 543
ALIZ SAPHIRE
ANTHRACENE DYE (ALIZ. SAPHIROL) SCH. 858
ACID BLUE G
M
VICTORIA BLUE B CCC
DI PHENYL NAPHTHYL METHANE DERIV SCH 559
ACID FAST VIOLET 6B NAC
TRI PHENYL METHANE DERIV SCH. 531
ACID VIOLET 5 B CONC
POSSIBLY M SCH. 530
FAST WOOL CYANONE 3R
METANILIC ACID → α NAPHTHYLAMINE → TOLYL PERIACID SCH. 257
DIRECT BLUE 8B CCC
H ACID ← BENZIDENE → H ACID SCH 337
INDULINE B CONC
SCH. 699
ACID BLUE BLACK EX CONS. NCW
ANILINE → H ACID → P NITRANILINE SCH 217
BUFFALO BLACK NBR
ANILINE → H ACID → P NITRANILINE SCH. 217
DIR BLACK EX. CONC CCC
PHENYLENEDIAMINE → BENZIDENE → H ACID ← ANILINE SCH 462
DUROL BLACK B NAC
LAURENTS ACID → NAPHTHYLAMINE → PHENYLPERIACID C.I. 307
ACID BLACK BX CCC
ANILINE → α NAPHTHYLAMINE → β ACID C.I. 267
100 HRS. MAY JUNE DIRECT SUNLIGHT FILTER.
85 HRS. HG. QUARTZ ARC THROUGH 1½ MM. CROWN GLASS
7.5 HRS. VIOLET FLAME ARC THROUGH GLASS GLOBE.
·6 HRS. DIRECT HG. QUARTZ ARC.

action in which the cotton itself played the part of a reducing agent. I was influenced in forming this hypothesis by the fact that Indanthrene Yellow G, which forms a blue leuco body, becomes green when exposed to the mercury arc and again becomes yellow when withdrawn from its influence; the first effect being clearly the result of the presence of the blue leuco substance mixed with unchanged dye, and the second to the disappearance of the blue leuco substance through oxidation back to the original yellow.

Harrison's Experiments and Conclusions

A search made through the files of the Journal of the Society of Dyers and Colorists soon revealed that exactly the same conclusion had been presented to that society by William Harrison on March 22, 1912. (See the July, 1912, number of the Journal of the Society.)

In a series of experiments made with dyes of different constitution, dyed on cotton or filmed on glass, and exposed to the mercury arc in sealed quartz tubes or to the sun in sealed glass tubes, Harrison was able to prove to his own satisfaction (a) that dyestuff is not affected by light alone, the presence of air or fiber, or both, being necessary for fading; (b) that azo dyes do not require air, but in intense light fade by contact with cotton alone; (c) that non-azo dyes—that is, dyes not capable of being destroyed by moderate reduction, are not permanently faded unless air is present, fading equally as well when filmed on glass as when dyed on cotton.

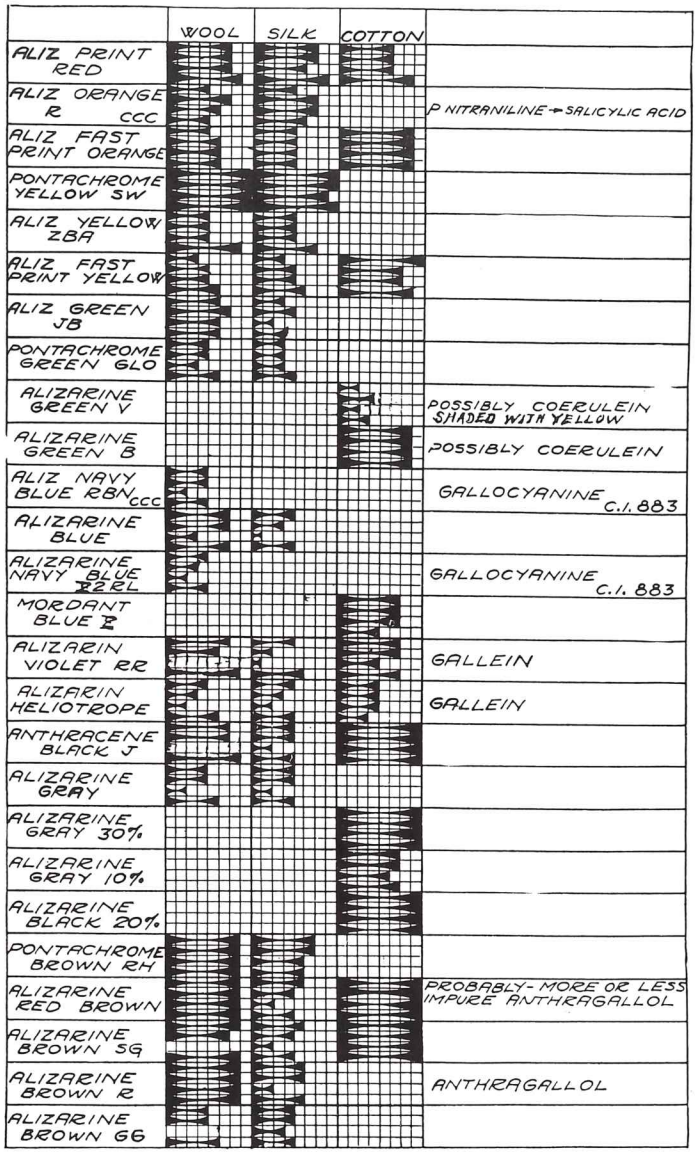
These observations, together with the results of tests showing the formation of oxycellulose in the cotton in contact with the faded dye, led him to conclude that the rapid fading of azo cotton dyes and similar easily reducible dyes was due to the reducing action of the cotton itself, and that the fading of non-azo dyes was mainly due to oxidation.

Oxidation Assists Reduction

Harrison also made this very important point, viz.; that the reducing action of cotton falls off rapidly with decrease of intensity of the fading light, and when the latter reaches the intensity of sunlight it practically disappears, so much so that direct cotton dyes require *indirectly* the assistance of oxygen in order to fade by sunlight.

He explains that cellulose in contact with direct cotton dyes under the influence of the sunlight is not sufficiently active to cause fading, but partially oxidized cotton is sufficiently active. In the ordinary fading of direct cotton colors under the action of sunlight, cotton is first changed into oxycellulose, which in turn acts reducingly upon the dyes.

In understanding what at first seems a paradox, it should be recalled that the behavior of oxycellulose with Fehling's solution shows that it has greater reducing power than cellulose itself, just as the oxidation products of alcohols—viz., the aldehydes—are more strongly reducing than the alcohols from which they



are derived. It is also known that in the oxidation of cotton, both soluble and insoluble substances with strong reducing powers are formed; the soluble part, penetrating the fiber, is able to carry the destructive reducing action into the interior of the fiber itself, so that the oxidation and reduction, which cause fading, need not necessarily be going on in exactly the same location in space.

The Unequal Acceleration of the "A" and "B" Action Explained

Returning to a consideration of the unequal accelleration of the "A" and "B" effects, which we now definitely identify as reduction and oxidation, it must be understood that an increase in fading intensity accelerates the oxidizing effect only slowly, or we may say in approximately arithmetic ratio because of the slight density of oxygen in the air; but when, with increased energy of fading, the stage is reached where the cellulose itself begins to act as a reducing agent, owing to its greater density and more intimate contact with the dye, its chemical effectiveness increases at a much greater rate than the activity of the oxygen—viz., in something like a geometric ratio. Hence we find that, with increasing intensity of a fading light, the dyes fading principally by reducing become relatively much more fugitive than those which fade mainly by oxidation.

This theory of fading is borne out by the results of a series of exposures made by Harrison on cotton dyed with direct and basic colors. In these exposures three grades of fading intensity are used, of which the sun represents the lowest, a 110-volt mercury arc the intermediate, and a 220-volt mercury arc the highest intensity. The dyeings were exposed as a group to each source of illumination until the most fugitive was almost completely destroyed by the particular light in question. The diagrammed results show that the reducible cotton dyes are progressing less fast as we pass from the sun fading to the 110-volt mercury arc fading, and from there to the 220-volt mercury arc fading. (See Am. Dyestuff Rep., Vol. XII, p. 294.)

A Limit to the Speed of Artificial Sun Fading

If the theory of the chemistry of fading just outlined is correct, there is a limit to the speed at which fading tests may be made with results which parallel those of sun fading. This limit is the fading intensity which starts a chemical action between the azo dyes and the cellulose. When this limit is passed, there is bound to be a divergence between the "non-reducible" and "reducible" type of dye. Therefore, in correcting the anomalous behavior of the mercury arc it should be necessary, first of all, to cut down its rate of action to something like that of sunlight.

Following out this idea, a set of fading tests was made to show the comparative effect of sunlight, mercury arc light applied directly, and mercury arc light moderated by filtering through 1¼ mm. of crown glass.

A selection of typical direct and basic colors dyed on cotton was exposed together so as to register on each swatch just forty-eight hours of winter sunlight. They were then exposed respectively to one-half hour and to one hour of direct mercury arc light, and finally to twenty hours of mercury arc light tempered by crown glass, the results of these exposures being registered on different parts of the same strip of dyed cotton. The length of time of the exposure through glass was regulated so as to make the resulting fade on the Scarlet 8BS indicator strip balance the sunlight fade. The outcome of this series of exposures confirmed the theory of fading in a very complete and satisfactory manner. When the indicator dyeing had been brought to an even fade with sunlight, it was found that all the other dyeings, both basic and direct, were likewise in almost perfect balance. Incidentally, the untempered arc fadings registered on the same swatches show conspicuously the reversals in fading characteristic of direct and basic colors exposed to rapid fading. The case of Bismarck Brown, a basic azo dye, is especially interesting. Corresponding to its reducible nature, it is seen to be much more affected by the direct mercury arc than are the non-azo basic colors. (See diagram, Am. Dyestuff Rep., Vol. XII, p. 295.)

Fading of Colors on Silk and Wool

The fact that direct cotton colors, even Congo Red, are much faster on silk and wool than on cotton tends to show that animal fibers do not exert as much reducing action as cotton. Therefore, the problem of equalizing the fading of the reducible and non-reducible dyes on animal fibers should be even easier of solution.

A set of dyeings on silk and wool made principally with acid colors but containing some direct colors, and at least one basic color, was suitably exposed and made to register 100 hours of May and June sun, 85 hours of 220-volt mercury arc through crown glass, 75 hours of carbon arc through glass and 6 hours of direct untempered mercury arc. The May and June sun was allowed to act direct, exposures being made in the middle of the day from 9:00 to 3:00 and an accurate tally kept. The distances of the mercury and carbon arcs were respectively 9 and 11 inches. The times of exposure to the different sources of artificial light were determined in each case by the course of the fading, the exposure being terminated on all samples when the larger proportion of the fadings balanced the corresponding sun fadings.

A study of these results shows, among other things, that dyed wool and silk faded with the untempered mercury arc exhibit fewer anomalies than dyed cotton faded in the same way. It is interesting, however, to note that dyes of the triphenyl methane type, both basic and acid, show a retardation similar to but not as great as the retardation of triphenyl methane basic colors on cotton.

The results show also that the temperered mercury arc fadings are somewhat more uniform than those of the violet carbon arc, although either one might be said to give a sufficiently close approximation to the true sun fastness. It is noticeable that the carbon arc, unlike the mercury arc, produces an acceleration in the fading of the triphenyl methane dyes rather than a retardation. It is a question whether the greater irregularity of the carbon arc fadings over the tempered mercury arc fadings may not be due to the somewhat excessive heat generated, the energy dissipated from the carbon arc being some three or four times greater than the energy from the mercury arc. That high temperature should influence fading is quite to be expected when we consider that most dyes are decomposable hydrates.

The results of this set of tests have been tabulated in Fig. 3. In this table (also in Figs. 4 and 5) the shaded area which shows the result of a particular fading represents residual dye. Where the shading covers eight of the small squares, the indication is that no fading was noticeable.

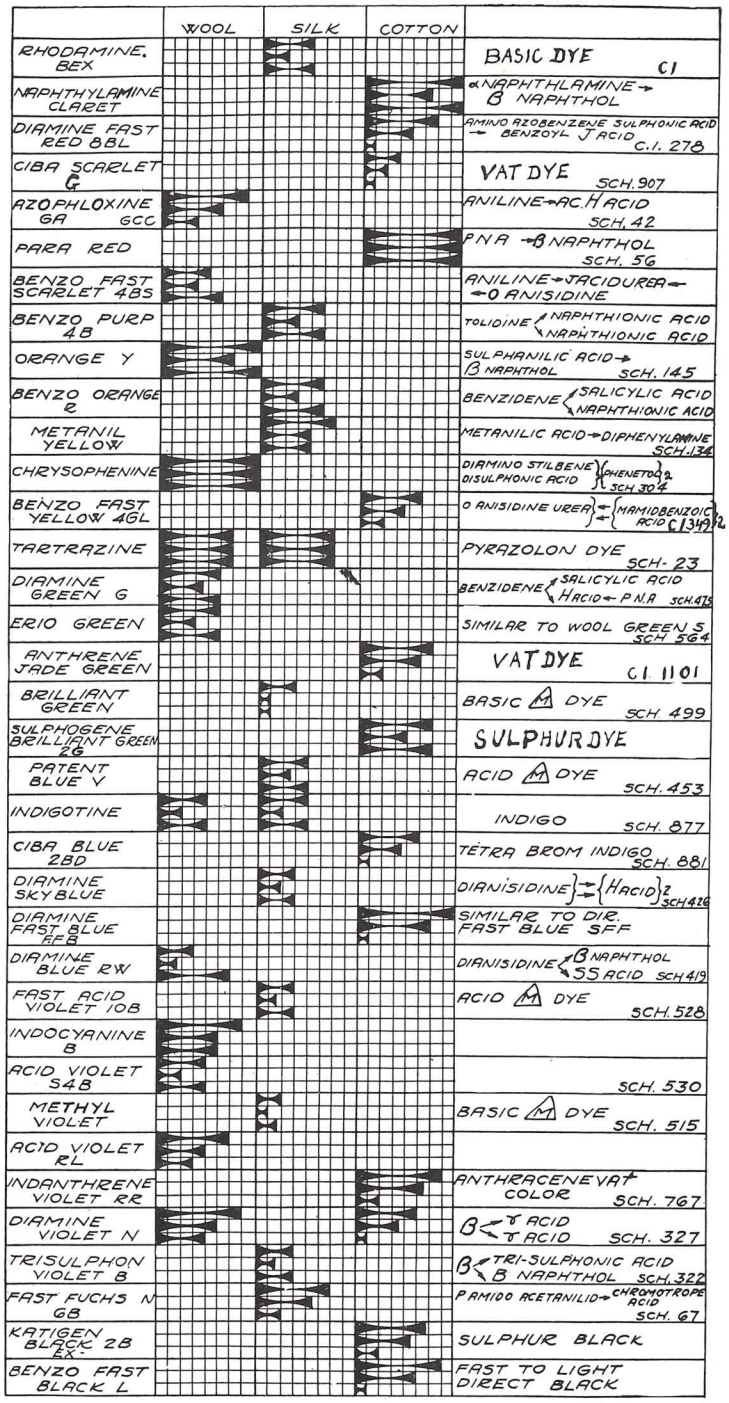
Chrome Colors Dyed on Wool, Silk and Cotton

Knowing the rather remarkable influence of certain metals on the fastness of dyes, it was felt to be desirable that the effect of tempering the mercury arc should be tested on chrome colors. A number of such colors dyed on wool and silk and printed on cotton were subjected to the same sort of exposures as the dyes just described, the exposure times, distances, etc., being exactly the same. Nothing remarkable, however, was noted in this connection except possibly even greater irregularities in the results of the carbon arc exposure. (See Fig. 4.)

An Assortment of Dyes on Cottons, Silk and Wool

While these tests were in progress we received an assortment of dyeings consisting of direct, acid, basic, sulphur, vat and ice colors dyed on appropriate fibers. These dyeings had been exposed so that they registered an equal but unknown number of hours of sunlight.

We were expected to expose the dyeings to both the tempered and untempered mercury arc so as to produce a general average of balanced fading. Unfortunately, it was assumed by the young man operating the fading cabinet that they had had 100 hours of sun. He started his tempered arc exposures with this in mind, and did not discover his mistake until seventy-five hours of tempered arc fading had been registered. The fading with the direct mercury arc was carried on more circumspectly and terminated at four hours with a fair


WOOL
SILK
COTTON
RHODAMINE BEX
BASIC DYE C1
NAPHTHYLAMINE CLARET
α NAPHTHLAMINE → β NAPHTHOL
DIAMINE FAST RED 8BL
AMINO AZOBENZENE SULPHONIC ACID → BENZOYL J ACID C.I. 278
CIBA SCARLET G
VAT DYE SCH. 907
AZOPHLOXINE GA GCC
ANILINE → AC. H ACID SCH. 42
PARA RED
PNA → β NAPHTHOL SCH. 56
BENZO FAST SCARLET 4BS
ANILINE → JACIDUREA → O ANISIDINE
BENZO PURP 4B
TOLIDINE { NAPHTHIONIC ACID / NAPHTHIONIC ACID
ORANGE Y
SULPHANILIC ACID → β NAPHTHOL SCH. 145
BENZO ORANGE R
BENZIDENE { SALICYLIC ACID / NAPHTHIONIC ACID
METANIL YELLOW
METANILIC ACID → DIPHENYLAMINE SCH. 134
CHRYSOPHENINE
DIAMINO STILBENE DISULPHONIC ACID { PHENETOL SCH. 304 } 2
BENZO FAST YELLOW 4GL
O ANISIDINE UREA { MAMIDOBENZOIC ACID C.I. 349 } 2
TARTRAZINE
PYRAZOLON DYE SCH. 23
DIAMINE GREEN G
BENZIDENE { SALICYLIC ACID / H ACID → P.N.A SCH. 475
ERIO GREEN
SIMILAR TO WOOL GREEN S SCH. 564
ANTHRENE JADE GREEN
VAT DYE C.I. 1101
BRILLIANT GREEN
BASIC M DYE SCH. 499
SULPHOGENE BRILLIANT GREEN 2G
SULPHUR DYE
PATENT BLUE V
ACID M DYE SCH. 453
INDIGOTINE
INDIGO SCH. 877
CIBA BLUE 2BD
TETRA BROM INDIGO SCH. 881
DIAMINE SKY BLUE
DIANISIDINE { H ACID } 2 SCH. 416
DIAMINE FAST BLUE FFB
SIMILAR TO DIR. FAST BLUE SFF
DIAMINE BLUE RW
DIANISIDINE { β NAPHTHOL / SS ACID SCH. 419
FAST ACID VIOLET 10B
ACID M DYE SCH. 528
INDOCYANINE B
ACID VIOLET 548
SCH. 530
METHYL VIOLET
BASIC M DYE SCH. 515
ACID VIOLET RL
INDANTHRENE VIOLET RR
ANTHRACENE VAT COLOR SCH. 767
DIAMINE VIOLET N
β { γ ACID / γ ACID SCH. 327
TRISULPHON VIOLET B
β { TRI-SULPHONIC ACID / B NAPHTHOL SCH. 322
FAST FUCHS N GB
P AMIDO ACETANILID → CHROMOTROPE ACID SCH. 67
KATIGEN BLACK 2B EX
SULPHUR BLACK
BENZO FAST BLACK L
FAST TO LIGHT DIRECT BLACK
100 HRS. MAY JUNE DIRECT SUNLIGHT
72 HRS. HG QUARTZ ARC THROUGH 1/4 MM CROWN GLASS FILTER
4 HRS. DIRECT HG QUARTZ ARC.
M = TRI PHENYL METHANE OR SIMILAR DERIVATIVES.

degree of balance, which would seem to indicate that the samples should have had about fifty-six hours of tempered arc fading, rather than seventy-five hours.

The principal interest of this set is in the presence of sulphur, vat and ice colors not included in the other sets. Making allowances for over-exposures, it will be seen that these dyes behave quite uniformly under the tempered arc. It is also interesting to note the fact that the vat colors in the set are not remarkably fast even to sunlight. (See Fig. 5.)

Commercial Samples of Silk

As a practical test for the effectiveness of the mercury arc tempered with crown glass, a set of commercial samples furnished by a large silk-dyeing concern was subjected to a balanced fading test. On examining these fadings it will be seen that in every case the eighty-five hours of tempered arc fading match the one hundred hours of May and June sun fading with sufficient closeness to give a true index of the relative fastness of the dyeings.

Further Improvements in the Tempered Mercury Arc

In fading, we are concerned with the chemical ractions between the dye and the fiber (or its oxidation products more particularly in the case of cotton) and with the oxidation of the dye itself.

Now, while theoretically all light has chemical effect, the dyed fabric, the atmosphere, and the photographic plate are all affected most by the ultra-violet, and then in a rapidly lessening degree by the violet and blue, the action of green, yellow, orange and red being negligible.

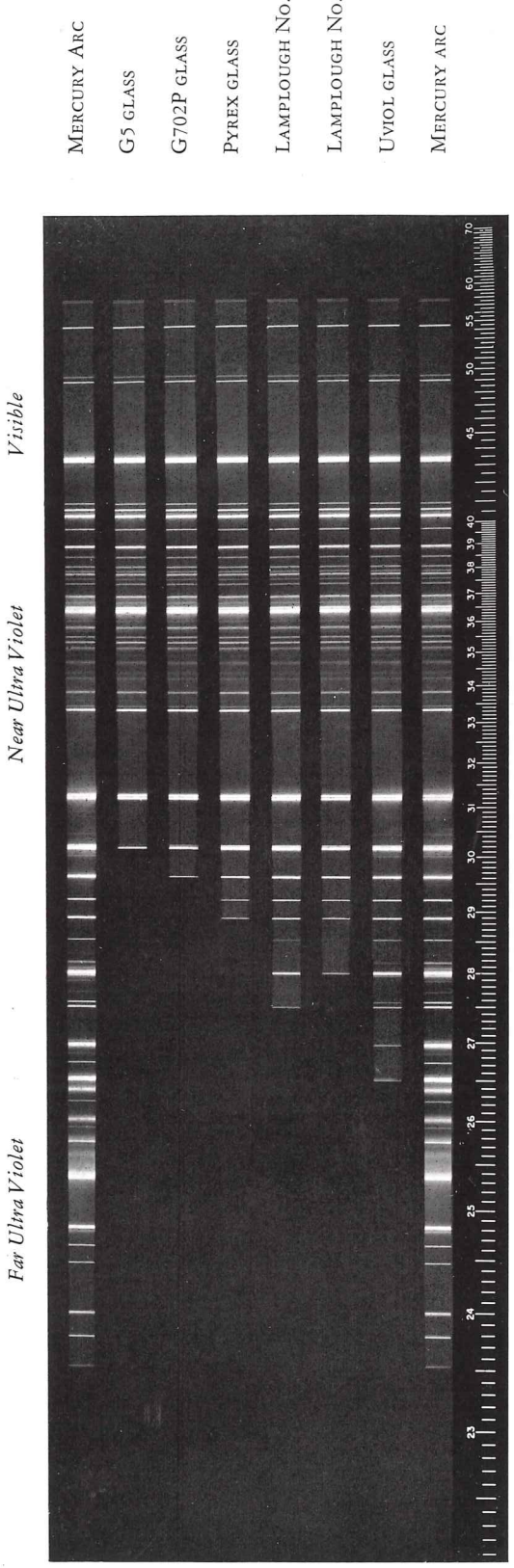
The photograph of the spectrum of the mercury arc shows a bright band in the region of the blue. The light which causes this band delivers its chemical energy to dyes which absorb it, and thereby increases to a slight degree their liability to fade. Hence, the mercury arc should, even in its tempered form, show a somewhat increased action on the dyes which absorb the blue and a lessened action on those which transmit it, and there seems to be evidence of some slight effect of this kind in the fadings recorded in the tables. In several instances in the tempered arc fadings, greens blues and violets (the dyes which transmit a certain propor-

tion of blue) show a relative retardation.

With the possibility of further increasing the value of the tempered mercury arc as a source of artificial fading light, we have decided to try the effect of eliminating this blue line altogether by means of a filter tinted with the oxides of cobalt and nickel (see Fig. 4). A series of fadings are now being prepared which will show the effect of the mercury arc tempered by a filter of this description. The results of this series of tests we hope to have ready some time in the near future.

Equalizing the Intensity of the Mercury Arc

Among other improvements in the operation of the mercury arc is the method by which the fall in ultra-violet intensity due to the mellowing of the lamp is corrected. This mellowing or aging takes place principally during the first 500 hours of operation. It has been found that starting a new 220-volt lamp with 160 volts drop in the arc proper and increasing the voltage drop at the rate of 2 volts per 100 hours of operation during this period of mellowing compensates almost exactly for the falling off in fading power of the tempered arc due to this aging. After the first 500 hours no further change is necessary during the remaining several thousand hours of the life of the lamp.



THE ACTION OF LIGHT ON COLOURING MATTERS

WM. HARRISON

* * * * * * *

It is well known that all colouring matters are acted upon by light to an extent depending on the nature of the colouring matter, the nature of the fibre on which it is dyed, and the composition of the atmosphere in which the dyed fibre is exposed.

To explain the facts known with regard to the action of light, many theories have been put forward. . . . . .

* * * * *

However, none of the theories put forward up to the present explain all the facts known with regard to the action of light on colours.

Owing to the difficulty of obtaining sunlight when desired, many attempts have been made to employ artificial light.

Vongerichten employed the Uviol or ultraviolet mercury lamp, and stated that good results could be obtained.

A. Walther in 1906 (*Färb. Ztg.,* March 1st, 1906) used the Heraeus or quartz mercury lamp, but concluded that the light from this lamp had a different action to sunlight on colours.

Scheurer (*Bull. Soc. Ind. de Mul.,* p. 324, 1910), in experimenting with the mercury lamp, showed that with Indigo the ozone which was formed by the light was not the factor which caused the colour to fade. He also found that glass absorbed the active rays. His general conclusions were the same as those of Walther.

Gebhard (*Färb. Ztg.,* pp. 6 and 26, 1911, this *Journal,* 1911, p. 133) proposed to use two lamps —one a mercury lamp, to provide the light of short wave length, and the other an ordinary arc lamp, to supply the light of long wave length. In discussing this (this *Journal,* p. 129, 1911), the author stated that it would probably be necessary to determine the composition of the light which constituted sunlight in various regions, and if possible to form a light of similar composition.

Later (this *Journal,* p. 198, 1911) the author showed by an experiment on Flavanthrene that light of high intensity had not the same effect on colours as light of low intensity, from which it was concluded that any attempt to shorten the time of exposure would lead to wrong results, and it would be necessary to adjust the intensity of the artificial light to be somewhat similar to that of the sunlight which falls on the patterns in the usual way of testing.

On account of the comparatively small cost of light from the mercury lamp and the rapidity of its action, experiments were undertaken to ascertain to what extent its action differed from that of sunlight, so that modifications could be made to adapt this light for the testing of the fastness of colors. For this purpose two lamps were tried, a small Heræus mercury lamp working with 110 volts 4 amperes, or 220 volts 2 amperes, and a large Westinghouse mercury lamp working with 220 volts 3.5 amperes. The patterns were placed 25 cms. from the source of light, and arranged round the lamp so as to utilize as much of the light as possible. A small fan was used to keep the apparatus cool and to remove the ozone formed. The light from the mercury lamp is extremely dangerous to the eyes, producing a painful complaint, and eventually may cause blindness. For this reason the lamp must be enclosed in a case. Neither the light nor the illuminated patterns should be looked at except through a thick sheet of glass, which absorbs the ultraviolet light.

The results are given in the annexed tables, and it will be seen that the large lamp has more than twice the activity of the small lamp. The large lamp, however, gives out much more heat, and this might account for some of the difference. The patterns exposed to the large lamp would have a temperature somewhat similar to that which would be produced by sunlight on a bright summer's day.

The results given in Tables 1 and 2 show what when colours are exposed to the small lamp, which bleaches many of the direct colours six times as quickly as sunlight, the order in which the patterns fade is not the same as with sunlight. Further, that when the large lamp, acting six or eight times as quickly as the small lamp, is used, the order of fading is again different. This is seen from the results in Table 3.

The degree of fading was judged by the eye, so as to get the patterns as nearly as possible in the order of fading. For this purpose ten degrees were taken, 0 representing "no fading" and 10 "colour completely destroyed." As the tests were made with the object of comparing the action of artificial and natural light, and not of comparing the fastness of the colours relative to one another,

the colours were dyed without regard to percentage of colour or depth of shade.

* * * * *

The results show an interesting effect; with the four yellows tested, Cotton Yellow and Chrysophenine are faster to sunlight than Thioflavine and Auramine. With light from the small lamp the four colours were practically of the same fastness, whilst with the large lamp which gave light of high intensity, Thioflavine and Auramine were faster than the other two. The colours thus show exactly opposite comparative fastness in the large lamp as in sunlight.

This is further proof of my statement that light of high intensity does not act relatively the same on all colours as light of low intensity.

As far as has been ascertained, basic colours appear to fade more slowly in mercury light than direct colours.

Since the mercury light afforded a rapid and convenient means of investigating the action of light, it was used for this purpose, and many important facts have been ascertained.

It is known that in the fading of many colours oxygen is absorbed, and it is generally understood that colours do not fade under the influence of light in the absence of air or oxygen. It is therefore concluded that oxygen is necessary for the fading of dyestuffs.

Gebhard states that reduction cannot possibly take place, since the fading occurs under the influence of light, in the absence of any possible reducing agent. However, there are many cases where the colour or substance present on a fabric is certainly reduced under the influence of light. For instance, on cotton, chromates and bichromates are reduced to chromium chromate (CrO_2), ferric and cupric chlorides are reduced to ferrus and cuprous chlorides. At the same time the cotton is oxidised, oxycellulose being formed. It may be argued that the oxygen of the air plays some part in the above reactions, first forming hydrogen peroxide with the moisture of the air, which then reacts with the substances present on the fibre, with liberation of oxygen.

However, Flavanthrene is reduced on cotton when exposed to light, and the green dihydroflavanthrene is formed. The effect of hydrogen peroxide on this dye has been tried under very variable conditions, but no reduction was observed. It is evident that hydrogen peroxide or ozone can play no part in the fading of this dyestuff. The question which naturally presents itself is, where is the reducing agent? The only possible place is within the fibre. To prove this, samples of several direct colours and Flavanthrene were dyed on cotton and exposed to mercury light until faded, when the direct colours were stripped off, and the pattern dyed with Methlylene Blue. The Flavanthrene sample was allowed to oxidise in air, and then padded with caustic soda and steamed. In all cases the exposed portions were found to contain oxycellulose.

However, a sample of undyed cotton exposed for the same length of time was also found to contain oxycellulose, so that no definite conclusions could be drawn from the experiments. Knecht (private communication), when experimenting with sunlight, found similar results, both the dyed and undyed samples containing oxycellulose in the exposed parts.

In investigating the action of light and air on cellulose, it was found that in addition to oxycellulose, some organic substances soluble in water and of an acid nature were formed, and these were quite strong reducing agents; they reduced Fehling's solution and ammoniacal silver nitrate quite readily. In addition to these, carbon dioxide appears to be formed.

The importance of this decomposition of the cellulose will be seen later.

Since the direct exposure of dyed patterns failed to afford any definite conclusions, other means were resorted to.

It has been shown by many authors that dyed materials do not fade when exposed to sunlight in evacuated glass tubes, or in tubes containing inert gases, and it was important to know whether the same applied to exposure to mercury light. As ultra-violet light is obsorbed by glass, it was necessary to use quartz tubes when using the mercury light. The results with sunlight were first verified by exposing samples of cotton dyed with Diamine Sky Blue FF, Crystal Violet, and Indigo to sunlight in evacuated glass tubes, and in tubes containing air and nitrogen. All the samples faded in air, but not in nitrogen or in vacuo.

Samples of cotton dyed with the same colours were next sealed up in quartz tubes in vacuo, in air, and in nitrogen, and exposed to mercury light. The direct colour was faded to practically the same extent in all three tubes; the basic colour and the Indigo were faded in air, but not in vacuo or in nitrogen.

To verify the effect obtained with the direct colour, samples of cotton were dyed with Benzo-violet and sealed up in quartz tubes containing respectively air, nitrogen, hydrogen, carbon dioxide, and a vacuum. On exposure to mercury light, the colour was found to be bleached to practically the same extent in all the tubes. A similar effect is shown with picric acid on cotton.

The vacuum was obtained by means of a Sprengel pump, and the tubes were left in connection with the vacuum gauge overnight to see that there was no leakage, and then sealed off and exposed. Every precaution was therefore taken to ensure the absence of gas. In filling the tubes with other gases, the tubes were exhausted, filled with the gas in

question and again exhausted, this process being repeated eight or ten times before finally filling the tubes. There is practically no possibility of any air being left in, unless some was absorbed by the fibre or colour.

Evidently the gas plays little or no part in the fading produced by mercury light on the direct colours tried, but oxygen is necessary for the fading of many basic colours. However, oxygen may take part in the fading of some direct colours.

As the direct colours faded in a vacuum, a means of determining the part played by the fibre presented itself. Samples of undyed cotton and cotton dyed with Diamine Sky Blue FF were exposed side by side in an evacuated quartz tube. When the dyed pattern was bleached, the samples were taken out and the undecomposed colour stripped off by means of hydrosulphite.

On dyeing with Methylene Blue the exposed portions gave the test for oxycellulose, slightly with the undyed sample, and strongly with the dyed sample. It appears, therefore, that the fibre is oxidised by the dyestuff, which must itself be reduced.

In the case of Flavanthrene also, the fibre was oxidised and the colour reduced when exposed in an exacuated quartz tube to mercury light, and some interesting points were noticed in carrying out this experiment. In the first part of the experiment the light was of low intensity, and the colour was turned to a yellowish green in about an hour, but no further change was noted after five hours' exposure. The intensity of the light was then increased, and the colour became green in about an hour, but again no further change was noted after prolonged exposure. It would appear that the reducing power of the cellulose increased with the intensity of the light.

On exposing the same dye in air to mercury light, no change was produced by light of low intensity, the rate of oxidation by the air being evidently greater than the rate of reduction by the fibre under the influence of the light. With light of high intensity the colour was reduced.

These experiments with Flavanthrene afford an explanation of the different actions of sunlight and mercury light. The fibre under the influence of sunlight, which contains only a few rays of low intensity which are absorbed by the fibre, would be a comparatively weak reducing agent and not strong enough to reduce many of the reducible colours whilst under the influence of powerful ultraviolet rays the fibre would be a powerful reducing agent and woulld readily reduce those colours.

A similar experiment to that described with Flavanthrene was carried out with Methylene Blue. A sample of cotton was padded with a solution of Methylene Blue, dried, and then exposed. In sunlight and ultraviolet light of low intensity the colour faded slowly, and apparently by oxidation, since the colour did not return on spotting with a solution of ammonia. In very intense ultraviolet light the colour faded very rapidly but returned on spotting with ammonia, showing that the colour was reduced. This experiment shows that increasing the intensity of ultraviolet light accelerates the reducing action of the cellulose more than the oxidising action of the air. This explains why attempts to shorten the time of exposure fail to give comparative results, since some dyes are oxidised and others reduced, and possibly some undergo both oxidation and reduction.

The same acceleration of the reducing action of the cellulose might be produced by sunlight concentrated by means of a lens, but this has not yet been ascertained.

Having determined the action of the fibre and the combined action of fibre and air, experiments were carried out to ascertain whether the colours faded in the absence of fibre or of fibre and air. In these experiments glass plates were painted with solutions of pure colouring matters and exposed to mercury light in air; at the same time a glass tube was painted with the same solutions, sealed up in an evacuated quartz tube and exposed with the plates.

In air the direct colours, Diamine Blue 2B and Benzopurpurine 4B, were unaffected; Flavanthrene was unaffected; also the acid colours, Picric Acid and Carminic Acid. The basic colours, Crystal Violet, Crystal Violet free base, and Methylene Blue, the sulphonated basic colour, Alkali Blue, and the sulphide colour, Immedial Sky Blue, were all faded to a considerable extent. Crystal Violet picrate faded much more rapidly than Crystal Violet hydrochloride.

In vacuo no visible fading was produced with any of the colours. (Crystal Violet picrate was not tested). The results show that certain colours, direct and acid, are bleached by mercury light in the absence of air, but in the absence of the fibre these colours are unaffected. In sunlight the direct colours fade slowly or not at all in the absence of air.

Other colours, basic, &c., are bleached in the absence of the fibre, but not in the absence of air.

Attempts were made to ascertain experimentally what happened to the dyestuffs during exposure. For this purpose simple compounds were used—metadinitrobenzene and picric acid. Solutions of these substances in alcohol were padded on cotton, dried, and exposed to mercury light. Picric acid changed to an orange-brown colour; this was thought to be due to the formation of picramic acid, which is what is generally supposed to be formed. No proof of this was obtained. Metadinitrobenzene changed to a brown colour; this was thought to be due to the formation of metanitraniline, but none could be found. Metanitraniline was then similarly exposed, and this changed to a brown

colour but not metaphenylene diamine was found. Metaphenylene diamine exposed in a similar manner also went brown presumably by oxidation. Both metanitraniline and metaphenylene diamine when exposed to the light on a glass plate, turned brown, the latter more than the former. Metadinitrobenzene exposed on a glass plate was unaffected. It was concluded from the above experiments that nitro groups would be reduced by the fibre and amido groups oxidised by the air, or by nitro groups if these were present. The last conclusion is supported by the fact that the picrate of Crystal Violet fades much more rapidly than the hydrochloride. The reactions undergone by the dyestuff would form a separate subject for research even with a single dye.

It is known that most direct colours fade more quickly when dyed on cotton than when dyed on wool, but as far as is known to the author no explanation for this has been offered. Since Flavanthrene affords a rapid and convenient means for detecting reducing action, samples of wool and cotton were dyed with this dye and exposed. The cotton pattern rapidly became green, the wool pattern very slowly. Wool then is not such a powerful reducing agent as cotton under the influence of light; reducible colours must therefore fade more rapidly on cotton than on wool. One would expect that basic colours would be faster on cotton than on wool, since the cotton would absorb more of the oxygen, which causes the fading. This appears to be the case with Methylene Blue, Safranine and Brilliant Green, but the reverse is the case with Magenta. However, the tannic acid on the cotton may have some effect, but this has not been carefully investigated.

The part played by wool in the fading of colours dyed upon it has not yet been investigated; the complex nature of this fibre renders such an investigation very difficult. There is one interesting point which may be mentioned. Light, a least light from the mercury lamp, rapidly turns wool brown and causes it to smell somewhat like burnt wool. Silk also is turned brown by the light, and even when pure is rapidly tendered.

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The accelerating effect of organic acidic substances on the rate of fading is very important, since it has been found that substances of a similar nature are produced by the action of light and air on cellulose.

Both oxycellulose and hydrocellulose cause reducible colours to fade more rapidly than cellulose.

An explanation can now be offered for many important facts known with regard to the action of light on dyed materials. For instance, it is known that colours do not fade, or fade only very slowly, when exposed to sunlight in a vacuum. This means that under the influence of sunlight, cellulose is not a sufficiently powerful reducing agent to reduce the colours. But when exposed to light in air the cellulose is converted into oxycellulose and other substances of a reducing nature, and these substances under the influence of sunlight may be capable of reducing the colours. To prove this opinion samples of cellulose, hydrocellulose, and oxycellulose were dyed to the same shade with Flavanthrene and Diamine Sky Blue, and exposed in evacuated glass tubes to sunlight. In one month Flavanthrene had faded slightly on cellulose, but much more so on oxy- and hydrocellulose. With Diamine Sky Blue no fading was noticed with cellulose, but a slight fading was noticed with oxy- and hydrocellulose. After two months a very slight fading was noticed with cellulose, but a distinct fading with oxy- and hydrocellulose. This seems to show that in sunlight it is not the cellulose itself which causes the fading, but the products formed from it by the action of light and air.

Gebhard has quoted two interesting experiments. A sample of cotton dyed with direct colour was exposed for a long time to diffused daylight, but did not fade. This sample was then exposed to sunlight together with a sample previously unexposed. The previously exposed pattern faded much more rapidly than the previously unexposed pattern. Another sample was exposed to sunlight in a dry atmosphere, but did not fade; this sample was then exposed together with a sample previously unexposed. The former pattern faded much more rapidly than the latter. Gebhard concludes from these experiments that in diffused daylight, or in sunlight in dry air, the dyestuff forms peroxides with the oxygen of the air, and these peroxides are subsequently destroyed by the light. The existence of such peroxides is very doubtful, and the fact that cellulose can reduce colours under the influence of light makes it certain that if such peroxides did exist they could not exist in the presence of cellulose under the influence of light.

However, a better explanation can be offered. It is well known that curtains when exposed to light, even in a position where they never get direct sunlight, become tendered. It would be expected that oxycellulose would be formed, and probably other reducing substances. The same would occur when cellulose was exposed to sunlight in a dry atmosphere. The presence of these substances in the exposed samples would explain why the colours fade much more rapidly.

Gebhard only considers the dyestuff and the atmosphere to take part in the process of fading; the fibre is evidently considered only in so far as it spreads the dye over a large surface. But it is evident that the fibre plays a very important part. There are thus four things to be considered in problems on fading. The nature of the light, the colouring matter, the fibre, and the atmosphere.

Under the influence of light many possible reactions may occur:—

(1) The light may convert oxygen into ozone, and this or the oxygen itself may oxidise the dyestuff.

(2) The fibre may reduce the dyestuff.

(3) Or both these reactions may occur at the same time.

(4) The air or ozone may oxidise the fibre and produce substances more capable of reducing the dyestuff.

(5) The air or ozone may oxidise the dyestuff and produce a substance more easily reduced by the fibre or its oxidation products.

(6) The fibre may reduce the dyestuff or otherwise react with it to produce substances more easily oxidised by the air.

(7) The light may cause one portion of the colour molecule to react with another.

When other substances are present on the fibre or in the atmosphere, their action on all the above reactions must be considered.

The large number of possible reactions shows how great a problem it is to ascertain the cause of the fading of dyestuffs. However, there is a possibility of classifying dyestuffs according to the manner in which they are destroyed. Dyestuffs which fade by oxidation would fade in an atmosphere of air or oxygen in the absence of a fibre. Dyestuffs which fade by reduction would fade in a vacuum when dyed on the fibre in question. Dyestuffs which fade by intramolecular change would fade in a vacuum in the absence of either fibre or atmosphere.

The results obtained up to the present seem to show that none of the theories proposed are incorrect, but that each theory applies to only a limited number of dyestuffs, whereas it has been the general procedure of the authors to apply their theories indiscriminately to all dyestuffs.

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The experiments described give some idea of what a colour has to stand when under the influence of light. A colour to be fast to light must be fast to oxidation by ozone or oxygen under the influence of light, reduction by the fibre or its transformation products under the influence of light, and oxidation or reduction assisted by the impurities, fillings, &c., under the influence of light, as well as being of itself fast to light.

In conclusion, the author wishes to thank Prof. Gee for the electrical apparatus, Prof. Knecht for the interest he has taken in the work and for many valuable suggestions, and also Prof. Rutherford for kindly exposing patterns to radium emanation.

Summary.—It has been shown:—

1. That in agreement with the results of Walther and Scheurer, light from the mercury arc lamp does not act relatively the same as sunlight on all colours.

2. That mercury light of high intensity does not act relatively the same as that of low intensity.

3. That cellulose is decomposed by the action of light and air with formation of reducing substances.

4. That in a vacuum under the influence of mercury light cellulose acts as a reducing agent, and reduces Flavanthrene and many direct colours, the cellulose itself being oxidised.

5. That the reducing power of cellulose increases with the intensity of the mercury light.

6. That in a vacuum under the influence of sunlight cellulose has little reducing power, but hydrocellulose and oxycellulose reduce Flavanthrene and Diamine Sky Blue. This explains why direct colours do not fade in a vacuum under the influence of sunlight.

7. That most colours do not fade in the absence of fibre and air; direct colours do not fade in absence of fibre; basic colours do not fade in absence of air.

8. That basic colours usually fade by oxidation, but may fade by reduction under certain described conditions.

9. That under the influence of mercury light, wool is not as powerful a reducing agent as cellulose.

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